3 EDUCATIONAL MONOGRAPH

prepared from,

A General Method for Automatic Computation of
Equilibrium Compositions and Theoretical
Rocket Performance of Propellants 6

by
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NASA TN D-132, 1959

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FOREWORD

This Monograph was produced in a pilot program at Oklahoma State University in Stillwater, Oklahoma, under contract to the NASA Office of Technology Utilization. The program was organized to determine the feasibility of presenting the results of recent research in NASA laboratories and under NASA contract in an educational format suitable as supplementary material in classwork at engineering colleges. The Monograph may result from editing single technical reports or synthesizing several technical reports resulting from NASA's research efforts.

Following the preparation of the Monographs, the program includes their evaluation as educational material in a number of universities throughout the country. The results of these individual evaluations in the classroom situation will be used to help determine if this procedure is a satisfactory way of speeding research results into engineering education.

ABSTRACT

Calculation of chemical equilibria in a complex reaction system is carried out in an iterative manner on computers. For this purpose the basic equations expressing equilibrium conditions are arranged systematically. The equations are linearized. The linearized equations are solved by the Crout reduction method.

General equations are given for the determination of equilibrium temperature and composition at specified pressure and enthalpy. The procedures are illustrated with a reasonably complex reaction mixture.

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INSTRUCTOR'S GUIDE FOR MONOGRAPHS

1. Educational level of the Monograph--Senior or beginning graduate students.

2. Prerequisite course material--General familiarity with the thermodynamics of chemical equilibria, and numerical analysis.

3. Estimated number of lecture periods required--One hour of lecture, or none. This Monograph is suitable for use as an independent reading assignment.

4. Technical significance of the material--Illustrative of the practical usefulness of the abstract principles of equilibrium. Also illustrative of the steps involved in reduction to practice, as the mathematical procedures used are widely applicable.

5. How Monograph TD-1 can best be used--

    (a) It is suggested that approximately a one-hour lecture be given on the Monograph material.

    (b) It is suggested that the class be assigned the homework problem contained in the Monograph.

6. Other literature, Briefs, or Monographs of interest--

    (a) V. N. Huff, Sanford Gordon, and V. E. Morrell, "General Method and Thermodynamic Tables for Computation of Equilibrium Composition and Temperature of Chemical Reactions", Report 1037, National Advisory Committee for Aeronautics, 1951.

    (b) F. J. Zeleznik and S. Gordon, "Calculation of Complex Chemical Equilibria", Ind. Eng. Chem. Fourth Annual State of the Art Symposium on Applied Thermodynamics, Washington, D. C., June 12-14, 1967.

7. Who to contact for further information--Technology Utilization Officer, Lewis Research Center, Cleveland, Ohio.

8. Note to Instructor: Only the uncolored pages of the instructor's Monograph are contained in the students' copies.

CALCULATION OF COMPLEX CHEMICAL EQUILIBRIA

Calculation of chemical equilibria in complex reaction systems has been much studied in connection with rocket propulsion. The combustion products in a rocket flow through the engine at very high temperatures. The calculation of theoretical rocket performance is based on chemical equilibrium conditions being maintained in the combustion chamber and in the nozzle. In view of the rapid rates of reaction at the prevalent high temperatures, the assumption of equilibrium appears to be a reasonable basis for theoretical analysis.

Equations expressing chemical equilibria are in general highly complex and non-linear. Explicit mathematical solution of these equations is usually not feasible. All general methods of calculation of complex chemical equilibria use an iterative technique (1, 2, 3, 4). Initial estimates are made for the unknowns and corrections to these estimates are obtained from the linearized form of the equations. The results are checked to determine if they satisfy the equilibrium conditions within a specified tolerance. If not, estimates of further corrections are made and the process repeated until convergence is achieved.
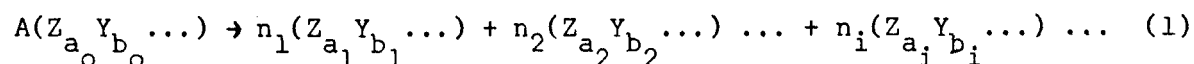
The following discussion will concern the method of Gordon, Zeleznik, and Huff (1), as it is highly developed and large computer programs are available upon request for its execution.

The salient features of this method of calculation are as follows:

1. Chemical equilibria are written for the compounds in relation to their constituent atoms -- a feasible scheme due to the high temperatures of interest.

2. The thermodynamic state of the system is specified by assigning the pressure and the enthalpy for adiabatic combustion calculations. Other thermodynamic quantities may be specified depending on the problem.

3. A linear set of equations is obtained from a Taylor series expansion of the chemical equilibrium equations.

4. Corrections are applied to all constituents.

5. Condensed reaction products can be formed.

6. Gas mixture is considered ideal.

Dissociation Equations

The total reaction under consideration may be written

$$A(Z_{a_o} Y_{b_o} \ldots) \rightarrow n_1(Z_{a_1} Y_{b_1} \ldots) + n_2(Z_{a_2} Y_{b_2} \ldots) \ldots + n_i(Z_{a_i} Y_{b_i} \ldots) \ldots \quad (1)$$

where Z, Y, ... are chemical elements, and n_i denotes the equilibrium numbers of moles of the i th molecule or atom of the formula $Z_{a_i} Y_{b_i} \ldots$ The subscripts a_i, b_i, ... can take on only positive integral values or zero. a_o, b_o, ... are proportional to the total number of gram atoms of the elements Z, Y, ... in the reaction mixture. For example, for the reaction between 3 moles of ammonia (NH_3) and 2 moles of nitric acid (HNO_3), the expression

$$3NH_3 + 2HNO_3$$

is condensed into

$$H_{11} N_5 O_6$$
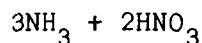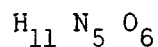
From this we make the identification

$$
\begin{array}{rcl}
Z & \to & H \\
Y & \to & N \\
X & \to & O \\
a_o & \to & 11 \\
b_o & \to & 5 \\
c_o & \to & 6
\end{array}
$$

The dissociation equations are written for the compounds in relation to their constituent atoms,

$$a_i Z + b_i Y + \ldots \to Z_{a_i} Y_{b_i} \tag{2}$$
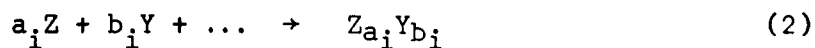
The partial pressures are related at equilibrium,

$$K_i = \frac{p_i}{p_Z^{a_i} p_Y^{b_i} \ldots} \tag{3}$$

The equilibrium constant K_i is expressed in terms of the standard free energy change ΔF_T^o,

$$\ln K_i = \left(\frac{-\Delta F_T^o}{RT} \right)_i \tag{4}$$

Mass Balance Equations

A mass balance equation may be written for each chemical element present.

$$Aa_o = \sum_i a_i n_i$$

$$Ab_o = \sum_i b_i n_i$$

$$\ldots \tag{5}$$

Total Pressure Equation

The total pressure P is the sum of the partial pressures,

$$P = \sum_i p_i \tag{6}$$

Enthalpy Balance Equation

The enthalpy balance equation states that enthalpy is conserved in the combustion reaction, i. e., the combustion process is adiabatic and not producing mechanical work. Let h_o denote the initial enthalpy per equivalent formula weight $Z_{a_o} Y_{b_o} \ldots$ of the fuel and oxidant,

$$h_o = n_f (H_T^o)_f + n_g (H_T^o)_g \tag{7}$$

Here n stands for the number of moles; and H_T^o, molar enthalpy at the initial conditions. Subscript f denotes fuel; and g, oxidant.

The enthalpy of the products of reaction is likewise based on one equivalent formula weight of the reactants,

$$h = \frac{1}{A} \sum_i (H_T^o)_i n_i \tag{8}$$

where $(H_T^o)_i$ is evaluated at the product conditions.

The enthalpy conservation equation states

$$h = h_o \tag{9}$$

at equlibrium conditions. Loss of heat during combustion can be accounted for by properly reducing h_o.

Deviation Equations for Specified p and H

At specified pressure and enthalpy, Equations (3), (5), (6), and (9) form the set of equations to be satisfied. These are rewritten into deviation equations.

We start by taking the logarithm of Equation (3),

$$\log p_i = a_i \log p_Z + b_i \log p_Y + \ldots + \log K_i \qquad (10)$$

The extent of deviation from Equation (10) by a set of trial values of the unknowns is expressed by δ_i defined by

$$\delta_i = \log p_i - a_i \log p_Z - b_i \log p_Y - \ldots - \log K_i \qquad (11)$$

The partial pressures can be replaced by the number of moles n_i, as

$$p_i = n_i \left(\frac{RT}{V} \right) \qquad (12)$$

For simplicity, set V = RT. It follows,

$$p_i = n_i \qquad (13)$$

This simplification is obtained at a price. Since V is fixed, A in Equation (1) is left as a variable for calculation.

Equation (11) becomes

$$\delta_i = \log n_i - a_i \log n_Z - b_i \log n_Y - \ldots - \log K_i \qquad (14)$$

Similarly, deviations from mass balances are derived from Equation (5),

$$\delta_a = Aa_o - \sum_i a_i n_i$$

$$\delta_b = Ab_o - \sum_i b_i n_i$$

$$\cdots \tag{15}$$

Deviation from the total pressure condition is expressed by

$$\delta_p = P_o - \sum_i n_i \tag{16}$$

Deviation from conservation of enthalpy,

$$\delta_h = Ah_o - \sum_i (H_T^o)_i n_i \tag{17}$$

Correction Equations

A direct solution of Equations (14) through (17) is usually not feasible. The Newton-Raphson method for solving non-linear simultaneous equations is used here.

Consider a simple example in two independent variables. Let y_1 and y_2 be functions of x_1 and x_2,

$$y_1 = f_1 (x_1, x_2)$$
$$y_2 = f_2 (x_1, x_2)$$

Upon expanding the functions in a Taylor series about the solution point (x_1^o, x_2^o) where both y_1^o and y_2^o are zero, and ignoring derivations of higher than the first order,

$$y_1 = y_1^o + \frac{\partial f_1}{\partial x_1} \Delta x_1 + \frac{\partial f_1}{\partial x_2} \Delta x_2$$

$$y_2 = y_2^o + \frac{\partial f_2}{\partial x_1} \Delta x_1 + \frac{\partial f_2}{\partial x_2} \Delta x_2$$

As (x_1^o, x_2^o) is the solution point, $y_1^o = 0$, $y_2^o = 0$. It follows,

$$y_1 = \frac{\partial f_1}{\partial x_1} \Delta x_1 + \frac{\partial f_1}{\partial x_2} \Delta x_2$$

$$y_2 = \frac{\partial f_2}{\partial x_1} \Delta x_1 + \frac{\partial f_2}{\partial x_2} \Delta x_2$$

Δx_1 and Δx_2, which approximate the corrections to be applied to current estimates of x_1 and x_2, can be computed from y_1 and y_2 which are the current deviation variables. New estimates of x are formed,

$$(x_1)_{r+1} = (x_1)_r - \Delta x_1$$

$$(x_2)_{r+1} = (x_2)_r - \Delta x_2$$

Following this procedure the simultaneous Equations (14) through (17) are linearized, and the signs of the deviation variables are changed so that the incremental variables can be __added__ to current variables to give new estimates.

$$x_i - a_i x_Z - b_i x_Y - \ldots - q_i x_T = -\delta_i \qquad (18)$$

$$\begin{bmatrix} \sum_i a_i n_i x_i - A a x_A = \delta_a \\ \\ \sum_i b_i n_i x_i - A b x_A = \delta_b \\ \ldots\ldots\ldots \end{bmatrix} \qquad (19)$$

$$\sum_i n_i x_i = \delta_p \qquad (20)$$

$$\sum_i h_i' x_i - A h x_A + T C' x_T = \delta_h \qquad (21)$$

where the correction variables and deviation quantities are written in logarithmic form,

$$x_i = \Delta \log n_i$$

$$x_Z = \Delta \log n_Z$$

$$\cdots\cdots\cdots$$

$$x_A = \Delta \log A$$

$$\delta_a = A \, a \log \frac{a_o}{a}$$

$$\cdots\cdots\cdots$$

$$\delta_p = P \log \frac{P_o}{P}$$

$$\delta_h = A \, h \log \frac{h_o}{h}$$

$$q_i = \left(\frac{\Delta H}{RT}\right)_i = \frac{\partial \log K_i}{\partial \log T}$$

$$h_i' = (H_T^O)_i \, n_i$$

$$C' = \sum_i (C_p^O)_i \, n_i$$

The new estimates for the $(r + 1)$ th iteration are obtained from the r th iterative values,

$$\log (n_i)_{r+1} = \log (n_i)_r + x_i$$

$$\log (A)_{r+1} = \log (A)_r + x_A \qquad\qquad (22)$$

$$\log (T)_{r+1} = \log (T)_r + x_T$$

The use of logarithms insures positive values for the estimates at all iterations.

The number of unknowns exactly balances the number of equations. Suppose the reaction system contains m chemical species (including the gaseous atoms). There are m equations of the type of Equation (18), but k of these are trivial where k denotes the number of chemical elements. This leaves (m - k) non-trivial equations. Adding these to the k equations of the type of Equation (19), one equation of pressure, and one equation of enthalpy, one counts a total of (m + 2) equations. There are just as many unknowns: m mole numbers, A, and T.

Matrix Construction

Equations (18) to (21) are solved most conveniently by means of matrix construction and reduction. The effort of solution is greatly economized by noting the special form of the matrix of interest.

A coefficient matrix is constructed and shown in Figure 1. The order of the columns is

(a) x_i of compounds

(b) x_i of free atoms

(c) x_A

(d) x_T

The order of the rows is

(a)   Dissociation equations in same order as the compounds in columns

(b)   Mass-balance equations in order of atoms in columns

(c)   Total pressure equation

(d)   Enthalpy balance equation

Figure 1 also contains the left hand side of the equations as the last column. The entire figure thus makes up the so-called "augmented matrix".

Matrix Reduction by the Crout Method

One of the best methods of solving simultaneous linear equations is given by Crout (5), and is described in the usual texts such as F. B. Hildebrand: Introduction to Numerical Analysis. The method is particularly adapted to application to the present set of equations because of the appearance of a large unit matrix at the upper left corner of the augmented matrix. The procedure of solution is as follows.

The original augmented matrix can be written

$$\left[\begin{array}{c|c} U_m & \alpha_1 \\ \hline \alpha_2 & \alpha_3 \end{array}\right]$$

where U_m denotes the unit sub-matrix. The Crout method when applied to this matrix is equivalent to replacing $[\alpha_3]$ with $[\alpha_4]$

$$\left|\begin{array}{c|c} U_m & \alpha_1 \\ \hline \alpha_2 & \alpha_4 \end{array}\right|$$

The sub-matrices U_m, α_1, and α_2 remain unchanged. $[\alpha_4]$ is the auxiliary matrix of the augmented matrix $[\alpha_5]$ formed by

$$\alpha_5 = \left[\begin{array}{c|c} \alpha_2 & \alpha_3 \end{array}\right] \left[\begin{array}{c} -\alpha_1 \\ \hline U_K \end{array}\right] \tag{23}$$

The values of the variables $x_{m+1} \cdots x_{n+1}$ are found from $[\alpha_4]$ by the process of back substitution given by Crout. The values of the remaining variables are found from the matrix equation

$$
\begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_m \end{bmatrix} = - [\alpha_1] \begin{bmatrix} x_{m+1} \\ \cdot \\ \cdot \\ \cdot \\ x_{n+2} \\ -1 \end{bmatrix} \tag{24}
$$

A Numerical Example of Combustion Reaction at Specified p and H

1 mole of liquid diborane (B_2H_6) at 298.16°K is burned with 5 moles of liquid oxygen bifluoride (OF_2) at 128.3°K in a rocket engine. The combustion chamber is kept at 20.4 atmospheres. Calculate the adiabatic combustion temperature and the composition of products.

An equivalent formula of the reactants is $Z_{a_o} Y_{b_o} X_{c_o} W_{d_o} = H_6 B_2 F_{10} O_5$ and $a_o = 6$, $b_o = 2$, $c_o = 10$, and $d_o = 5$.

The enthalpy values of the reactants are

$$ H^o{}_{B_2H_6} = 570.149 \text{ Kcal/mole} $$

$$ H^o{}_{OF_2} = 67.077 \text{ Kcal/mole} $$

It follows,

$$ h_o = 570.149 + 5\,(67.077) = 905.534 \text{ Kcal/equivalent formula} $$

which must also be equal to the enthalpy of the products.

Experience shows that, in addition to the atomic gases H, B, F, and O, the chemical species BF_3, B_2O_3, BF, BH, BO, B_2, H_2, H_2O, OH, HF, O_2, F_2 should be considered and included in the calculation.

For a first estimate of the combustion conditions, we set

$$T = 4000°K, A = 1.000$$

$$n_i = 1.000$$

for all chemical species participating in reaction.

It turned out that these estimates deviate substantially from the converged solution. Yet convergence was achieved in six iterations.

The thermodynamic properties of the reactants and products at 4000°K are calculated and shown in Table I.

The matrix of correction equations is constructed, and shown in Figure 2. The steps are as follows:

(1) Negative values of a_i, b_i, c_i, and d_i are entered under x_H x_B x_F x_O, one gaseous molecule in a row. The gaseous molecule for the row is indicated by a 1 entered under the chemical symbol of the molecule.

(2) Negative values of $q_i = \left(\dfrac{\Delta H}{RT}\right)_i$ from tables of thermodynamic functions are entered in the column x_T. In this case they are obtained from Table I.

(3) Elements of the "constant" column are computed

$$\delta_i = \log n_i - a_i \log n_H - b_i \log n_B$$
$$- c_i \log n_F - d_i \log n_O - \log K_i$$

The values of $\log K_i$ are obtained from tables of thermodynamic properties, in this case Table I. Because all molecules and atoms are estimated

to be 1, their logarithms vanish so that

$$\delta_i = - \log K_i$$

in Figure 2. All logarithms are to the base of 10.

(4) The estimated values of n_i are entered in the next to last row.

(5) Elements in the four rows of Equation (19), except those in columns x_A and x_T, are constants in the equations of atomic balance. The first row in this category expresses hydrogen balance; the second, boron balance; etc.

(6) Elements of the last row, except those on columns x_A and x_T are obtained by multiplying n_i by the values of $(H_T^o)_i$ from tables of thermodynamic functions, in this case Table I. For example, the entry in the first column is $72172 \times 1.000 = 72{,}172$. All entries in this row have been divided by 10^5.

(7) Elements of column x_A on rows marked Equations (19) and (20) are obtained by summing elements to the left in each row and changing the sign of the total.

(8) The element of the x_T column on the row marked Equation (21) is computed by $T \sum_i (C_p^o)_i \, n_i$. The values of the $(C_p^o)_i$ are obtained from tables of thermodynamic functions, in this case Table I.

(9) Values of the constant column are obtained as follows:
On rows marked Equation (19), the value already entered in the x column is -Aa. With the estimated value of A = 1.000,

$$a = \frac{Aa}{A} = \frac{8.000}{1.000} = 8.000$$

$$\delta_a = Aa \log \frac{a_o}{a} = 8.000 \log \frac{6}{8.000} = -0.999$$

The values of δ_b, δ_c, δ_d, and δ_h are found in a similar manner.

(10) The constant column of the row marked Equation (20) is found as follows: The sum of the elements of row p is the pressure P = 16.000; δ_p is computed from the formula

$$\delta_p = P \log \frac{P_o}{P} = 16.000 \log \frac{20.4}{16.000} = 1.688$$

The matrix of Figure 2 is now used to find values for the x's. Applying Crout method, the matrix is partitioned into sub-matrices as indicated by the dotted lines. The matrix multiplication

$$[\alpha_2 \mid \alpha_3] \begin{bmatrix} -\alpha_1 \\ \hline U_k \end{bmatrix}$$

results in matrix $[\alpha_5]$ shown in Figure 3(a). Crout's auxiliary matrix corresponding to $[\alpha_5]$ may then be constructed and is shown in Figure 3(b) and the values of x_H, x_B, x_F, x_O, x_A, and x_T are shown in Figure 3(c). The values of the remaining functions are computed from Equation (24), or equivalently by substitution into Equation (18). The solution is found to be

$$x_{BF_3} = 0.7056 \qquad x_{OH} = 0.4907$$

$$x_{B_2O_3} = -1.100 \qquad x_{HF} = 1.377$$

$$x_{BF} = 1.166 \qquad x_{O_2} = 0.1737$$

$$x_{BH} = 1.665 \qquad x_{F_2} = -2.037$$

$$x_{BO} = 0.6135 \qquad x_{H} = 1.299$$

$$x_{B_2} = -2.139 \qquad x_{B} = 0.9290$$

$$x_{H_2} = 0.03982 \qquad x_{F} = 1.222$$

$$x_{H_2O} = -0.7999 \qquad x_{O} = 1.459$$

$$x_{A} = 0.1232 \qquad x_{T} = 0.1544$$

These values are to be applied to the initial estimates for n_i, A, and T,

$$(\log n_i)_{\substack{second \\ estimate}} = (\log n_i)_{\substack{first \\ estimate}} + x_i$$

For example, the second estimate of n_{BF_3} would be

$$\log n_{BF_3} = \log 1.000 + 0.7056$$

$$n_{BF_3} = 5.077$$

The second estimates of n_i, A, and T are then used to set up new matrices according to the procedure described. The procedure is

repeated until the desired accuracy has been obtained. Six iterations were required to give the final values of n_i, A, and T for the illustrative example. The results are:

$$n_{BF_3} = 2.6593 \qquad n_{OH} = 0.6785$$

$$n_{B_2O_3} = 0.1235 \qquad n_{HF} = 7.1456$$

$$n_{BF} = 0.1936 \qquad n_{O_2} = 0.9210$$

$$n_{BH} = 0.0001 \qquad n_{F_2} = 0.0003$$

$$n_{BO} = 0.1669 \qquad n_H = 1.7694$$

$$n_{B_2} = 0 \qquad n_B = 0.0577$$

$$n_{H_2} = 0.1271 \qquad n_F = 1.3043$$

$$n_{H_2O} = 0.0627 \qquad n_O = 5.1903$$

$$A = 1.6622 \qquad T = 4775.5°K$$

HOME PROBLEM STATEMENT

Calculate the equilibrium composition of air (N_8O_2) at 4000°K and 1.4 atomspheres. Consider the molecular species N_2, O_2, and NO to be at dissociation equilibrium with the elemental gases N and O.

The constants of dissociation equilibrium at 4000°K are given below:

	log K
N_2	2.5138
O_2	-0.3818
NO	0.5395

Simplify the method of calculation presented in the text to adapt to the present case of fixed temperature. Reorganize the necessary correction equations into matrix form and carry out the solution.

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Table I

Thermodynamic Properties of Participants in

$B_2H_6 + 5 F_2 O$ Reaction

at 4000°K.

Product, Equivalent Formula	$(H_T^o)_i$ kcal/mole	$(\Delta H_T^o/RT)_i$	$(S_T^o)_i$	$(C_p^o)_i$	log K_i
BF_3	72.172	-62.0753	105.951	19.738	5.6953
B_2O_3	233.435	-80.5932	116.760	25.660	5.1094
BF	262.961	-17.2884	73.904	8.905	1.6342
BH	356.994	- 8.3004	61.412	8.826	-2.6110
BO	252.739	-18.1834	69.620	9.065	1.0327
B_2	572.053	- 7.9892	70.580	8.923	-2.7625
H_2	99.593	-13.9385	51.054	9.151	-0.4061
H_2O	57.706	-29.2092	72.458	13.300	-0.3470
OH	76.560	-13.6031	63.989	9.165	-0.1668
HF	32.016	-19.6736	61.054	9.045	1.8944
O_2	37.310	-15.3125	70.783	9.932	-0.3804
F_2	96.012	- 8.7047	70.813	9.451	-3.1373
H	105.192	----	40.306	4.968	----
B	317.778	----	49.549	4.968	----
F	82.601	----	51.230	4.974	----
O	79.493	----	51.479	5.091	----

	Equation	Compounds			Atoms			x_A	x_T	Constant
		x_1	x_2	----	x_Z	x_Y	----			
	(18)	1	0	0	$-a_1$	$-b_1$	--	0	$-q_1$	$-\delta_1$
		0	1	0	$-a_2$	$-b_2$	--	0	$-q_2$	$-\delta_2$
		0	0	--	--	--	--	0	--	--
a	(19)	$a_1 n_1$	$a_2 n_2$	--	n_Z	0	--	$-Aa$	0	δ_a
b		$b_1 n_1$	$b_2 n_2$	--	0	n_Y	--	$-Ab$	0	δ_b
--		--	--	--	0	0	--	--	0	--
p	(20)	n_1	n_2	--	n_Z	n_Y	--		0	δ_p
h	(21)	h'_1	h'_2	--	h'_Z	h'_Y	--	$-Ah$	TC'	δ_h

Figure 1. Augmented Matrix of Linearized Correction Equations for Determination of Chemical Equilibria at Assigned Pressure and Enthalpy.

Gaseous Molecules   Atoms

Equation	x_{BF_3}	$x_{B_2O_3}$	x_{BF}	x_{BH}	x_{BO}	x_{B_2}	x_{H_2}	x_{H_2O}	x_{OH}	x_{HF}	x_{O_2}	x_{F_2}	x_H	x_B	x_F	x_O	x_A	x_T	Constant
(18)	1	0	0	0	0	0	0	0	0	0	0	0	0	-1	-3	0	0	62.075	5.695
	0	1	0	0	0	0	0	0	0	0	0	0	0	-2	0	-3	0	80.593	5.109
	0	0	1	0	0	0	0	0	0	0	0	0	0	-1	-1	0	0	17.288	1.634
	0	0	0	1	0	0	0	0	0	0	0	0	-1	-1	0	0	0	8.300	-2.611
	0	0	0	0	1	0	0	0	0	0	0	0	0	-1	0	-1	0	18.183	1.033
	0	0	0	0	0	1	0	0	0	0	0	0	0	-2	0	0	0	7.989	-2.763
	0	0	0	0	0	0	1	0	0	0	0	0	-2	0	0	0	0	13.939	-0.406
	0	0	0	0	0	0	0	1	0	0	0	0	-2	0	0	-1	0	29.209	-0.347
	0	0	0	0	0	0	0	0	1	0	0	0	-1	0	0	-1	0	13.603	-0.167
	0	0	0	0	0	0	0	0	0	1	0	0	-1	0	-1	0	0	19.674	1.894
	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	-2	0	15.313	-0.380
	0	0	0	0	0	0	0	0	0	0	0	1	0	0	-2	0	0	8.705	-3.137
(19)	0	0	0	1.000	0	0	2.000	2.000	1.000	1.000	0	0	1.000	0	0	0	-8.000	0	-0.999
	1.000	2.000	1.000	1.000	1.000	2.000	0	0	0	0	0	0	0	1.000	0	0	-9.000	0	-5.879
	3.000	0	1.000	0	0	0	0	0	0	1.000	0	2.000	0	0	1.000	0	-8.000	0	-0.775
	0	3.000	0	0	1.000	0	0	1.000	1.000	0	2.000	0	0	0	0	1.000	-9.000	0	-2.297
(20)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0	0	1.688
(21)	.721	2.334	2.629	3.569	2.527	5.720	.995	.577	.765	.320	.373	.960	1.051	3.177	.826	.794	-27.346	6.446	-13.125

Figure 2. Numerical Example of Correction Equations for Adiabatic Combustion of Diborane and Oxygen Bifluoride After First Estimate of n_i, A, and T.

x_H	x_B	x_F	x_O	x_A	x_T	Constant

$$
\begin{bmatrix}
12.000 & 1.000 & 1.000 & 3.000 & -8.000 & -127.873 & 1.391 \\
1.000 & 13.000 & 4.000 & 7.000 & -9.000 & -283.010 & -16.322 \\
1.000 & 4.000 & 16.000 & 0 & -8.000 & -240.597 & -13.564 \\
8.000 & 7.000 & 0 & 17.000 & -9.000 & -333.400 & -17.383 \\
8.000 & 9.000 & 8.000 & 9.000 & 0 & -294.871 & -3.866 \\
8.854 & 28.736 & 7.861 & 12.414 & -27.346 & -454.757 & -7.663
\end{bmatrix}
$$

(a) Matrix $[\alpha_5]$ Obtained From Matrix Multiplication

$$[\alpha_2 \mid \alpha_3] \begin{bmatrix} -\alpha_1 \\ \overline{v} \\ k \end{bmatrix}.$$

$$
\begin{bmatrix}
12.000 & 0.08333 & 0.08333 & 0.2500 & -0.6667 & -10.656 & 0.1159 \\
1.000 & 12.917 & 0.3032 & 0.5226 & -0.6451 & -21.085 & -1.273 \\
1.000 & 3.917 & 14.729 & -0.1560 & -0.3263 & -10.004 & -0.5902 \\
3.000 & 6.750 & -2.297 & 12.364 & -0.2745 & -14.727 & -0.8487 \\
8.000 & 8.333 & 4.807 & 3.395 & 13.210 & -4.857 & 0.8731 \\
8.854 & 27.998 & -1.366 & -4.644 & -5.102 & 172.652 & 0.1544
\end{bmatrix}
$$

(b) Matrix $[\alpha_4]$ (Crout's Auxiliary Matrix of $[\alpha_5]$).

x_H	x_B	x_F	x_O	x_A	x_T
1.299	0.9290	1.222	1.459	0.1232	0.1544

(c) Values of Corrections (Crout's Final Matrix).

Figure 3.   Numerical Example of Solution of Correction Equations
by Matrix Methods.

PROBLEM SOLUTION

Since temperature is fixed, Equation (21) will no longer be needed. The quantities δ_h, q_i, h_i' and c' defined on page 8 all drop out. The last row of the matrix in Figure 1 should be deleted; the same applies to the column marked x_T.

The calculation may be started by making the first estimate that all the species are present to the extent of 1 mole and the total number of moles is also 1 mole. In spite of some gross errors in these estimates, convergence to a high degree of approximation is achieved in three iterations. The time required for hand calculation amounts to about five hours.

The correction equations based on the first estimates are arranged in matrix form in Figure 4. The calculations of the first iteration are shown in Figure 5. Similar results for the second iteration are shown in Figures 6 and 7; and for the third iteration in Figures 8 and 9.

It has been found worthwhile to keep up the check calculations recommended by Crout. The check columns in the above figures record the result of the check calculations.

Figure 10 shows the calculated compositions at the end of each iteration, including the final results.

Equation	Gaseous Molecules			Atoms			Constant
	x_{N_2}	x_{O_2}	x_{NO}	x_N	x_O	x_A	
(18)	1	0	0	-2	0	0	2.5138
	0	1	0	0	-2	0	-0.3818
	0	0	1	-1	-1	0	0.5395
(19)	2.000	0	1.000	1.000	0	-4.000	1.2041
	0	2.000	1.000	0	1.000	-4.000	-1.2041
(20)	1.000	1.000	1.000	1.000	1.000	0	-2.7642

Figure 4. Correction Equations for Homework Problem After First Estimate.

x_N	x_O	x_A	Constant		Check Column
6.000	1.000	-4.000	-4.36298		- 1.36298
1.000	6.000	-4.000	-0.98002		+ 2.01998
4.000	4.000	0	-5.43570		+ 2.56430

(a) Matrix $[\alpha_5]$ Obtained from Matrix Multiplication

$$[\alpha_2 \mid \alpha_3]\left[-\frac{-\alpha_1}{U_k}-\right].$$

x_N	x_O	x_A			Check Column
6.000	0.16667	-0.66667	-0.72716		- 0.22716
1.000	5.83333	-0.57143	-0.04335		+ 0.38522
4.000	3.33333	4.5714	-0.52118		+ 0.47882

(b) Matrix $[\alpha_4]$ (Crout's Auxiliary Matrix of $[\alpha_5]$).

x_N	x_O	x_{N_2}	x_{O_2}	x_{NO}	x_A
-1.0178	-0.3412	+0.4783	-1.0641	-0.8194	-0.5212

(c) Values of Corrections.

Figure 5.   Crout's Matrix Solution of Correction Equations of Homework
Problem — First Iteration.

Gaseous Molecules				Atoms			
x_{N_2}	x_{O_2}	x_{NO}		x_N	x_O	x_A	Constant
1	0	0		-2	0	0	0.00
0	1	0		0	-2	0	0.00
0	0	1		-1	-1	0	0.00
6.016	0	0.1516		0.0960	0	-6.2636	-2.5986
0	0.17254	0.1516		0	0.4354	-0.7595	-0.07644
3.008	0.08627	0.1516		0.0960	0.4354	0	-1.6282

Figure 6.   Correction Equations for Homework Problem — After First
Iteration.

x_N	x_O	x_A	Constant		Check Column
12.280	0.1516	-6.2636	-2.5986		+ 3.5694
0.1516	0.9321	-0.7595	-0.0764		+ 0.2478
6.2636	0.7595	0	-1.6282		+ 5.3949

(a) Matrix $[\alpha_5]$.

x_N	x_O	x_A	Constant		Check Column
12.280	0.01235	-0.51007	-0.21161		+ 0.29067
0.1516	0.93023	-0.73333	-0.04764		+ 0.21901
6.2636	0.68214	3.69510	-0.07314		+ 0.92686

(b) Matrix $[\alpha_4]$.

x_N	x_O	x_{N_2}	x_{O_2}	x_{NO}	x_A
-0.2477	-0.1013	-0.4953	-0.2026	-0.3490	-0.0731

(c) Values of Corrections.

Figure 7.   Solution of Correction Equations of Homework Problem —
Second Iteration

Gaseous Molecules				Atoms			
x_{N_2}	x_{O_2}	x_{NO}		x_N	x_O	x_A	Constant
1	0	0		-2	0	0	0
0	1	0		0	-2	0	0
0	0	1		-1	-1	0	0
1.923	0	0.06786		0.05427	0	-2.04513	-0.00399
0	0.10824	0.06786		0	0.3610	-0.5371	-0.01253
0.9615	0.05412	0.06786		0.05427	0.3610	0	-0.04435

Figure 8.   Correction Equations for Homework Problem After Second Iteration.

	x_N	x_O	x_A	Constant	Check Column
	3.96813	0.06786	-2.04513	-0.00399	+ 1.98687
	0.06786	0.64534	-0.5371	-0.01253	+ 0.16357
	2.04510	0.5371	0	-0.04435	+ 2.53785

(a) Matrix $[\alpha_5]$.

	x_N	x_O	x_A	Constant	Check Column
	3.96813	0.01710	-0.51539	-0.00101	+ 0.50071
	0.06786	0.64418	-0.77949	-0.01934	+ 0.20117
	2.04510	0.50213	1.44543	-0.02253	+ 0.97746

(b) Matrix $[\alpha_4]$.

x_N	x_O	x_{N_2}	x_{O_2}	x_{NO}	x_A
-0.0120	-0.0369	-0.0240	-0.0738	-0.0489	-0.0225

(c) Values of Corrections.

Figure 9.   Solution of Correction Equations of Homework Problem —
Third Iteration.

	First Estimate	After First Iteration	After Second Iteration	After Third Iteration— Final Results
A	1.000	0.3012	0.2545	0.2416
n_N	1.000	0.0960	0.05427	0.05279
n_O	1.000	0.4354	0.3610	0.3316
n_{N_2}	1.000	3.008	0.9615	0.9098
n_{O_2}	1.000	0.08627	0.05412	0.04566
n_{NO}	1.000	0.1516	0.06786	0.06064
p	5.000	3.777	1.49875	1.4005

Figure 10.   Calculated Results After Each Iteration.